V.K.6 Hydrogen Fuel Cell Development in Columbia (SC)*

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*Congressionally directed project

Objectives

- Development of metal-free oxygen reduction catalysts to reduce cost, facilitate manufacturing, and enhance durability of fuel cells (Barriers A-C; Task 2 electrodes).
- Development of redox stable mixed ionic and electronic conductors (MIECs) for bi-electrode supported cell (BSC) symmetrical solid oxide fuel cell (SOFC) designs, to reduce cost by simplifying manufacturing, enhance durability, and greatly reduce sensitivity to thermal cycling (Barriers A-C, G; Tasks 8-portable power, 11-innovative fuel cells, 10-long term failure mechanisms).
- Development of durable, low-cost seals for proton exchange membrane (PEM) stacks, through the establishment of laboratory characterization methodologies that relate to cell/stack performance (Barriers A, C; Task 6 Seals).
- Development of understandings and methodologies to establish hydrogen quality as it relates to PEM cell applications for transportation needs (Barriers B, C, G; Tasks 9-models for impurities, 8-portable operation).
- Development of a first principles multiphysics durability model based on interpretations of electrochemical impedance spectroscopy (EIS) data that link the multiphysics processes, the microstructure, and the material states, with cell impedance responses and global performance, mechanistically, as a foundation for engineering durability during design and manufacture of fuel cells (Barriers A-G; Tasks 9-models, 10-long term failure mechanisms, 11-innovative fuel cell design and manufacture).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Cost
(B) Durability
(C) Performance
(D) Water Transport within the Stack
(E) System Thermal and Water Management
(F) Air Management
(G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

Carbon-based catalysts: To develop non-precious-metal catalysts for PEM fuel cell with high selectivity and durability which perform as well as conventional Pt catalysts with a cost of at least 50% less than the target of 0.2 g (Pt loading)/peak kW.

SOFC materials: Develop SOFC electrode materials that enable direct operation on hydrocarbon fuels.

Carbon-based catalysts: Determine PEM seals materials that have no appreciable weight loss or leachants over a 60 week test period.

Hydrogen Contamination: Establish the rate and mechanism of NH_3 transport in PEM cells over a 60-week period; identify the species of sulfur contamination on Pt catalysts in the presence of various gas species, e.g., H_2O and O_2.

Multiphysics based durability modeling: Use impedance spectroscopy to identify specific material state change driven degradation mechanisms during SOFC operation.

Accomplishments

- Metal-free oxygen reduction catalysts have been developed to reduce cost, facilitate manufacturing, and enhance durability of PEM fuel cells.

- Redox stable MIECs for BSC symmetrical (and other) SOFC designs have been developed.
- The development of durable, low-cost seals for PEM stacks, through the establishment of laboratory characterization methodologies that relate to cell/stack performance.
- Understandings and methodologies have been developed to enable the establishment of hydrogen quality as it relates to PEM cell applications for transportation needs.
- The development of first principles multiphysics durability models based on interpretations of EIS data that form a foundation for engineering durability during design and manufacture of fuel cells have been constructed for BSC SOFC designs.

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Introduction

The activities of the present project are contributing to the goals and objectives of the Fuel Cells element of the Hydrogen, Fuel Cells and Infrastructure Technologies Program of the Department of Energy through five sub-projects. Three of these projects focus on PEM cells, addressing the creation of carbon-based metal-free catalysts, the development of durable seals, and an effort to understand contaminant adsorption/reaction/transport/performance relationships at low contaminant levels in PEM cells. Two projects address barriers in SOFCs; an effort to create a new symmetrical SOFC design with greatly increased durability, efficiency, and ease of manufacturing, and an effort to create a multiphysics engineering durability model based on EIS interpretations that associate the micro-details of how a fuel cell is made and their history of (individual) use with specific prognosis for long-term performance, resulting in attendant reductions in design, manufacturing, and maintenance costs and increases in reliability and durability.

Approach

- Work on a previous DOE project, DE-FC36-03GO13108, was leveraged to create new carbon-based, metal-free catalysts for oxygen reduction.
- Research under way in a partnership with NASA Glenn, Savannah River National Laboratory (SRNL) and ENrG Inc. is being leveraged to create a new symmetrical SOFC design with greatly increased durability, efficiency and ease of manufacturing.
- Recent advances at the University of South Carolina in controlled hydration and temperature characterization of polymer-based materials will be used to establish a methodology for characterization of materials in seals in PEM stacks.
- On-going work with the National Renewable Energy Laboratory, Argonne National Laboratory, SRNL, and Los Alamos National Laboratory forms a foundation for the work on developing an understanding of the contaminant adsorption/reation/transport/performance relationships at low contaminant levels in PEM cells.
- Conceptual foundations laid by research supported by the National Science Foundation and several industries including United Technologies Fuel Cells are being expanded to create a multiphysics engineering durability model based on EIS interpretations that associate the micro-details of how SOFCs are made and their history of individual use with long-term performance, to achieve reductions in design, manufacturing and operating costs.

Results

Only one example of salient results are presented in the limited space available here. Other results appear in the quarterly reports.

Mesoporous composite carbon-based metal-free catalysts are being developed under the direction of Prof. Popov. The goal of this project is to develop highly active and stable carbon-based metal-free catalysts and carbon composite catalysts with strong Lewis basicity (π electron delocalization) to facilitate the oxygen reduction reaction (ORR). New nitrogen-modified carbon composite catalyst was synthesized by pyrolyzing the cobalt- and iron-nitrogen chelate over a silicon dioxide (SiO_2) followed by a leaching and post-heat-treatment. The activity of the new catalysts were significantly enhanced which is attributed to the expected increase in the number of active sites. The stability optimization of the new catalysts is on going.

It was found that the presence of nitrogen, transition metal, and carbon is crucial to produce non-precious metal carbon-based catalysts for the ORR. The activity of these catalysts is promising; however, their stability is not comparable with the Pt counterpart. Typically, the catalyst performance significantly decreases as soon as fuel cell starts to operate despite the catalyst synthesis methods, membrane and electrode assembly (MEA) fabrication methods, and fuel cell operation conditions. In the present report, a new synthesis strategy was developed to increase the activity of the catalyst while maintaining its stability [1,2]. Figure 1 shows the polarization curves of PEM fuel cells using CC-SiO_2 and CC-Carbon catalysts, respectively. The cathode catalyst loadings are 2 mg cm^{-2}. The experiments were performed using 30 psi back pressure on both anode and the cathode. The CC-SiO_2 showed the current density

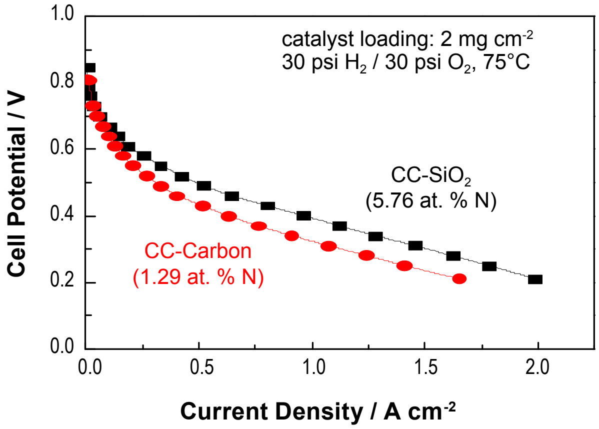

FIGURE 1. Current-voltage plot of PEM fuel cells using CC-SiO_2 and CC-Carbon catalysts at 75°C. The cathode catalyst loading was 2.0 mg cm^{-2}. The tests were run using H_2 and O_2 with back pressures of 30 psi/30 psi.

of 0.96 A cm^{-2} at 0.4 V and 1.98 A cm^{-2} at 0.2 V. The CC-Carbon showed the current density of 0.65 A cm^{-2} at 0.4 V and 1.65 mA cm^{-2} at 0.2 V. It is evident that the CC-SiO_2 showed higher catalytic performance than the CC-Carbon.

Conclusions and Future Directions

Future work includes the following tasks:

- Model the recovery of performance from contaminants such as sulfur.
- Improve the integrity of the carbon composite catalyst layer in the MEA.
- Measure the ionic conductivity of lanthanum strontium gallate magnesite pellets in different atmospheres and temperatures.
- Investigate compression set of seals for heating/cooling cycles; develop life prediction model.
- Complete button cell measurements to support EIS durability modeling.

Special Recognitions & Awards/Patents Issued

1. Prof. Ken Reifsnider, PI of this effort gave an invited keynote lecture at the ECS meeting in San Francisco in May, 2009.

2. The Crystal Flame Innovation Award in Research from FuelCell South was presented to Dr. Popov's research group for research work in the field of non-precious catalyst development and preparation thin film assemblies with nano-structured catalysts and the development of the pulse deposition technique for preparation of membrane electrode assemblies.

FY 2009 Publications/Presentations

1. Tan, J., Chao, Y.J., Wang, H., Van Zee, J.W., "Chemical and mechanical stability of EPDM in a PEM fuel cell environment," accepted for publication in Polymer Degradation and Stability, July 2009.

2. S. Park, B.N. Popov, Effect of cathode GDL characteristics on mass transport in PEM fuel cells, Fuel 88 (2009) 2068-2073.

3. N.P. Subramanian, X. Li, V. Nallathambi, S.P. Kumaraguru, H. Colon-Mercado, G. Wu, J.-W. Lee, B.N. Popov, Nitrogen-modified carbon-based catalysts for oxygen reduction reaction in PEM fuel cells", J. Power Sources 188 (2009) 28-44.

4. S. Park, B.N. Popov, "Effect of Hydrophobicity and Pore Geometry in Cathode GDL on PEM Fuel Cell Performance", Electrochim. Acta 54 (2009) 3473-3479.

5. H.-Y. Jung, S. Park, and B.N. Popov, "Electrochemical Studies of Unsupported PtIr Electrocatalyst as Bifunctional Oxygen Electrode in Unitized Regenerative Fuel Cell (URFC)", *J. Power Sources* 191 (2009) 357-361.

6. G. Liu, X. Li, B. N. Popov, "Stability Study of Carbon-Based Catalysts for Oxygen Reduction Reaction in Polymer Electrolyte Membrane Fuel Cells", *216th Meeting of the Electrochem. Soc.*, Vienna, Austria, October, 2009.

References

1. G. Liu, B.N. Popov, "Development of non-precious oxygen reduction catalysts from N-doped ordered porous carbon", Appl. Catal. B: Environ, in revision.

2. X. Li, S. Park, B.N. Popov, "Highly stable Pt and PtPd hybrid catalysts supported on a nitrogen-modified carbon composite for fuel cell applications", J. Power Sources (in press).